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COMPLETE SPECIFICATION

Improvements relating to Decorative Laminates

We, FORMICA INTERNATIONAL LIMITED, a British Company of, P.O. Box No. 2, De La Rue House, 84—86 Regent Street, London, W.1., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a decorative laminated plastics articles carrying a surface coating and to a process of making the same.

Decorative plastics laminates have obtained a wide acceptance as materials for use in surfacing articles of furniture such as tables, counters, kitchen units, school desks, domestic appliances and other items having a useable or working surface. They are also finding ever increasing application as materials for cladding vertical surfaces such as interior and exterior walls.

The virtue of such decorative laminates is to be found in their physical properties and to a slightly lesser extent in their chemical characteristics. High amongst the physical properties which make such products suitable for use on horizontal surfaces is abrasion resistance, which is increased by the incorporation in or on the surface of certain thermosetting synthetic resins. In one particular form of decorative laminate the surface resin is a melamine-formaldehyde resin, which is used to impregnate a sheet of alpha cellulose paper forming the outermost component of an assembly of resin-impregnated sheets from which the laminate is produced by the application of controlled heat and pressure for an appropriate period of time; beneath the impregnated alpha cellulose sheet is positioned a sheet of high quality printed or otherwise decorated paper which has itself been impregnated with a melamine-formaldehyde resin, a urea-formaldehyde resin or both, and which in the finished product is visible through the overlying alpha cellulose sheet, which is rendered transparent by the pressing operation. Thus the product has visual appeal on account of the decoration afforded by the print sheet, and acquires abrasion resistance from the overlying melamine-formaldehyde resin layer.

British Specification No. 874326 describes a decorative laminated plastics sheet which possesses an abrasion resistant surface which is not formed by a pre-formed thermosetting resin - impregnated overlay sheeet as described above. The result is achieved by applying to the print sheet a coating composition which comprises a thermosetting resin, finely divided silica and finely divided fibrous cellulosic material having a refractive index approximating to that of the cured resin, the composition being clear and highly translucent in its cured condition and comprising, for each 100 parts of the resin, from 5 to 30 parts of finely divided silica and from 10 to 40 parts of the finely divided fibrous material. (All "parts" are by weight.) The silica is preferably in the form of silica flour, having a maximum particle size of 6 microns, and the dry weight of the coating is between 0.022 and 0.033 lb./sq.ft. or between 108 and 160 g./sq. metre.

The prior specification describes adding to the coating a small quantity of a wet-tack reducing aid, for example sodium carboxy-methyl cellulose. Such compounds may be included in amounts of about 1 to 3% to improve the coatability of the compositions, their effect being allegedly to change the composition from a stringy tacky solution to one which breaks sharply and coats smoothly without substantially changing the viscosity. The specification gives some Examples in which a wet-tack reducing aid is included and others in which it is not; comparative test results indicate that the wear resistance of laminates coated with the composition is not increased, but may ac-

tually be decreased, when such compounds as sodium carboxymethyl cellulose are present, and the statement that the wet-tack reducing aids are included simply to facilitate processing appears thus to be confirmed.

We have now found that particularly and unexpectedly advantageous results are obtained by applying to the print sheet or other decorative layer a coating comprising a thermosetting resin and finely divided quartz. In particular we have found that the use of quartz enables the production of laminates having at the same time considerably higher abrasion resistance and greater print clarity (in the sense that the coating has a smaller obscuring or modifying effect on the appearance of the print pattern or design) than when other forms of finely divided silica are used. In addition completely satisfactory abrasion results are obtainable at lower coating weights than are used according to Specification No. 874326, and hence more cheaply. (the greater clarity is ascribable, at least in part, to the use of such lower coating weights and hence lower coating thicknesses.)

In one aspect therefore the invention comprises laminates which comprise a thermoset resin impregnated surface layer bearing a decorative pattern, such as a print sheet, carrying a coating consisting of a transparent thermoset resin in which is dispersed quartz with a maximum particle size of 50 microns and fibrous material of length not exceeding 100 microns and of refractive index similar to that of the thermoset resin such that the coating is transparent. The invention consists also in the production of such laminates by applying to a thermosetting resin impregnated sheet or layer carrying a decorative pattern a composition comprising the thermosetting resin, the quartz and the fibrous material and subsequently curing the said resin by subjecting a laminate assembly containing the coated sheet or layer to heat and pressure. The best results are obtained when the volatiles content of the coated resin-impregnated decorative layer is reduced to not more than 5%.

By "quartz" we mean this crystalline form of silica, as opposed to tridymite, cristobalite, coesite and keatite, in its natural state and in either or both of its α and β modifications.

Preferably the average size of the particles is not less than 2 microns and not more than 50 microns, size ranges of 3—40 microns, and especially 10—15 microns are preferred. The maximum particle size is not more than 50 microns. One particularly suitable material is that supplied by Croxton and Garry Limited under the trade designation "GAROQUAZ CML/2"; 61% of the aggregated particles of this material are less than 40 microns in diameter and, on complete dispersion, 90% of the particles are less than 30 microns, the average particle size being between 12 and 13 microns.

In contrast to the use of other forms of silica, as described in Specification No. 874326, we have found no processing disadvantages in the utilisation of ground quartz in which particles larger than 2 microns predominate. Indeed, while as stated above we prefer to use finely divided quartz of average particle size between 10 and 15 microns, the use of quartz still presents advantages when the average particle size is as low as and even lower than 5 microns. We have however found that when the average size falls to 3 microns and below, the print clarity and the abrasion resistance of the laminate are lower than when the average particle size is above 5 microns and especially within the preferred range of 10—15 microns.

As the thermosetting resin it is preferred to use a melamine-formaldehyde resin, but others may be used with good results, for example the condensation products of other aminotriazines or substituted aminotriazines and aldehydes, the condensation products of phenols and aldehydes, the condensation products of urea and aldehydes, and cross-linked polyesters.

For each 100 parts of resin there may be used for example 5 to 30 parts of quartz, and 10 to 40 parts of fibrous material particularly preferred proportions being 10 parts of quartz and 20 parts of fibrous material.

The finely divided fibrous material is advantageously cellulosic, and flock materials are further preferred; cotton flocks are particularly useful, but other suitable cellulosic materials include viscose rayon. The fibre length must not exceed 100 microns if an efficient dispersion is to be obtained, and although the best craze-resisance is obtained with fibres less than 10 microns long, the most generally satisfactory products are obtained with a fibre length between 30 and 50 microns.

The coating composition may include also a penetration control additive, which serves to limit the extent to which the resinous constituent penetrates the paper to which the composition is applied. The inclusion of such an agent has been found to improve the wear value for a given coating weight. While carboxymethylcellulose has some efficacy as a penetration control agent, the best results are obtained by the use of alginates, notably sodium alginate in an amount corresponding to between 0.1% and 2.0%, and preferably between 0.2% and 0.75%, of the total weight of the coating composition. Alginates not only exert a gelling influence on the compositions but also reduce the wetting capacity of the resin, while carboxymethylcellulose has only the first effect.

The coating composition is preferably applied to the print sheet or other decorative layer to provide a coating weight between 90 and 110 g. per square metre, and more particularly between 95 and 105g. per square metre.

The print sheet or other decoratively coated print must of course itself be impregnated with a thermosetting resin, e.g. a melamine-formaldehyde, a urea-formaldehyde or melamine-urea-formaldehyde resin. This impregnation is advantageously effected immediately before the application of the coating composition, the two steps being performed in such a manner that neither the coating composition as a whole nor any of its constituents penetrates the paper or other fibrous base material of the decorative layer to any substantial extent; this method gives laminates having the best abrasion resistance. Drying is preferably effected only after the coating operation, but two controlled drying stages may be used, one between impregnation and coating and the other after the coating operation. However, it is possible, to pre-impregnate and partially dry the print sheet before it is coated in a separate apparatus.

The finely divided fibrous cellulosic material may be any cellulosic fibrous material whose refractive index is substantially the same as that of the cured coating resin. In each and every case the fibrous material must have a refractive index which is such that the coating formed, after the application of the laminating heat and pressure, is clear and highly translucent. Some cellulosic flocks will impart to the laminate a yellowish discolouration, and are therefore best used, if at all, in association with an optical brightener, e.g. in amount up to 0.5% by weight of the coating composition; the addition of such an optical brightener to counteract yellowness and to restore the true colour of the underlying print sheet, is usually necessary only when the print sheet is of a light colour and the cellulose flock is not a cotton product.

The invention is illustrated by the following Examples. "Parts" and proportions are by weight.

EXAMPLE I

Resin The resin used in this Example for the coating was a spray dried melamine-formaldehyde resin having a melamine to formaldehyde mole ratio of 2 to 1. It was in the form of a fine white powder, readily soluble in water or alcohol-water mixtures to give a clear colourless solution having a solids content of 60% and a specific gravity of 1.25 and a shelf life of about 24 hours at room temperature. The pH of the solution was between 9.5 and 10.5.

Quartz The quartz employed was that supplied by Croxton Garry Limited under the trade designation GAROQUARZ CML/2. It has an average particle size of 12 to 13 microns and appears as a white finely divided powder.

Cellulosic Fibrous material

The cellulosic fibrous material was the finely divided cotton flock sold as "Hutchinson's Fine-Ground Cotton Flock". The particle size of the flocks is between 30 and 50 microns.

The following coating composition was made up using the above raw material and thoroughly mixing the ingredients.

	Parts
Melamine-formaldehyde resin	100
Garoquarz	10
Flock	20
Water	60

The resin was first dissolved in water at 30°—40°C., the quartz was then added slowly while the composition was stirred, and the flock was then added similarly, naturally cooling taking place throughout.

High quality titanium-dioxide-loaded untreated paper bearing a decorative printed pattern on one surface was impregnated with a 45% solids aqueous solution of a melamine-urea-formaldehyde resin of mole ratio 1:1.33:4, acquiring a dry resin content of about 35%.

The impregnated print paper was then coated at about 4ft./min. by application of the coating composition described above and then passed at the same speed through a drying oven 7 feet 6 inches long maintained at a temperature of about 150°C., the resulting impregnated and coated sheet which had a resin content of 35%, a coating weight of about 90 grams/sq. metre and a volatiles content of about 6.0%, was then subjected to a re-dry treatment for 2 hours at 50°C. to reduce the volatiles content to about 4.4%.

A print sheet of the required size was then cut from the roll and assembled as the top sheet of a laminate assembly the other sheets being six core sheets comprising 10 mill kraft paper impregnated with a 55% solution of a phenolformaldehyde resole and subsequently dried to a volatiles content of 6%, the resin solids of the core paper being 30%.

The assembly was pressed in a conventional way at 150°C. and under a pressure of 1400 psi, cooled to about 50°C. while still in the press, and removed in the form of a unitary decorated laminated plastics board.

EXAMPLE 2

In this Example the melamine resin used for the coating had a melamine to formaldehyde mole ratio of 2.2. to 1. It was used in aqueous solution, the solids content being 60% by weight, the pH about 9.0, the specific gravity 1.26 and the viscosity 54 seconds by the No. 4 Ford cup.

The coating composition had a solids content of 65% and the following (solids) composition:

	Parts
Melamine-formaldehyde resin	85
Sodium alginate (Manutex SX/RF)	0.5
Garoquarz CML/2	5.0
Flock	10.0

"Manutex" is a Registered Trade Mark.

The composition when used in the production of decorative laminated plastics sheets by following the processing conditions of Example 1 gave products having a coating weight of 90 g/square metre.

The laminates from Examples 1 and 2 were subjected to abrasion tests in accordance with the standards of the National Electrical Manufacturers Association (NEMA) Test LP2—1.06, the abrasion tapes being changed after 500 revolutions. The results are reported in the Table below and compared therein with the results obtained from similar runs in which silica flour of particle size 1—6 microns was used instead of the quartz, and also with a present day standard commercial product of the same general type.

Material under Test	Abrasion Revs	Abrasion Rate (gms per 100 revs)
Sample from Example 1	700 — 900	0.012 — 0.014
Sample from Example 2	900 — 1000	0.012 — 0.014
Commercial product	620	0.025
Sample using silica flour	640	0.035

"Abrasion revolutions" is the number of cycles of an abrasive covered wheel in contact with the test sample necessary for break through to occur. "Abrasion rate" is a measure of the number of grams of sample abraded off per one hundred revolutions. From the above Table it will be seen that the use of quartz instead of silica flour markedly increases the abrasion resistance, especially as shown by the abrasion rate. Moreover a comparison between the results obtained in Examples 1 and 2 demonstrates the benefit accruing from the presence of sodium alginate, presumably as a result of its efficacy in controlling the movement of the quartz particles away from the surface of the coating and towards the print sheet.

The improvements to be obtained from the use of finely divided quartz in place of silica flour is thus evident, surface wear rate being a most important parameter in decorative laminated plastics. One particular advantage of the very low wear rate obtained by the use of compositions according to this invention is that the weight of coating that must be applied to obtain the wear value demanded by the NEMA specification can be reduced, thus improving print clarity and reducing cost.

EXAMPLE 3—6

A series of experiments was carried out to determine the comparative effects of a series of penetration control additives. Laminates were prepared as described in Example 2, and the following results obtained, the abrasive tapes being changed after 200 revolutions.

Example	Additive	Amount wt. %	Total Solids Content	Revs/100g. of coating weight
3	None	0	68	430
4	Sodium carboxymethyl cellulose	1.6	68	485
5	Manutex SX/LD (Sodium alginate)	0.5	68	602
6	Manutex SX/LH (Sodium alginate)	0.5	62	655

From the above it can be seen that whereas the addition of sodium carboxymethyl cellulose has some efficacy in improving the wear value for a given coating weight, markedly better results are obtained by the addition of sodium alginate.

Example 7

A laminate having a light grey coloured print sheet was made in accordance with Example 2 but using a composition in which the "Hutchinson's Fine Ground Cotton Flock" was replaced by SOLKA-FLOC BW 200 ("SOLKA-FLOCK" is a Registered Trade Mark). This material, which is derived from wood pulp, is not less than 99% cellulose when dry, and is for practical purposes inert to acids, alkalis and solvents. The test results obtained in Example 2 were again obtained, but a general yellow discolouration of the print sheet was noticeable.

Example 8

Example 7 was repeated save that 0.5% of an optical brightener (UVITEX AB CONC - "UVITEX" is a Registered Trade Mark) was added to the coating composition. The print sheet in the finished laminate appeared entirely unblemished, and no discolouration was to be seen.

Example 9—12

Example 2 was repeated four times, save for the use in each case of another form of finely divided quartz in the place of GAROQUARZ CML/2. The results are reported below, the abrasive tapes being changed after 200 revolutions.

Example	Quartz	Particle Size in microns	Coating weight	Abrasion Resistance	
				Revs.	Rate gms/100. Revs.
9	GAROQUARZ CML/1	12 — 13 (average)	92 g.	480	.027
10	LQ QUARTZ	50 (maximum)	92 g.	500	.028
11	B200/400 QUARTZ	20 (average)	90 g.	400	.035
12	325 mesh QUARTZ	50 (maximum)	103 g.	570	.025

All these laminates had a good surface ap- 140 g. per square metre show no signs of crazing when they are flexed.

In general terms, we have found that as the concentration of fibrous material (flock) in the coating composition is reduced, the wear resistance falls also, but the rate of wear remains substantially unchanged; this indicates that the lower the flock concentration, the more readily the resin will be able to penetrate into the print sheet. We have also observed that the clarity and colour of the print sheet improve only slightly as the flock concentration decreases below the optimum value for wear resistance. As stated above the best concentrations of flock and quartz in coating compositions are generally in the neighbourhood of 20% and 10% respectively. Higher concentrations of quartz have no substantial further effect in increasing the abrasion resistance, but below 10% the effect falls off markedly. Laminates having a coating weight up to at least pearance and showed no milkiness, nor did they craze when flexed.

We have found also that the volatiles content of the print sheet has a marked effect upon the rate of wear of the finished laminate. The dry steps referred to in Example 1 are readily adaptable to produce material having a volatiles content between 3.5 and 5.0%, and as is evidenced from the Table below values within this range are necessary if the optimum rate of wear is to be obtained. However, unless the speed at which the web passes through the apparatus is reduced to an uneconomic level (say to 2ft./min.) a re-dry stage is essential. The effects of different re-dry treatments on one material are shown in the Table below; as usual the abrasive tapes were changed after 200 revolutions.

Re-dry Time	Volatiles content percent	Rate of Wear gms/100 Revs.
1 hr. at 80°C.	5.0	0.021
2 hrs. at 80°C.	4.4	0.022
3 hrs. at 80°C.	4.3	0.021
10 mins. at 100°C.	3.6	0.022
No re-dry	6.0	0.26

The foregoing Examples specify compositions which include either cotton or wood-pulp flocks, but while either is generally acceptable, a cotton flock has the advantages that it is less prone to discolouration and that laminates having a coating containing it tend to have better craze resistance than those in which the coating contains a wood-pulp flock.

WHAT WE CLAIM IS:—

1. A laminate comprising a thermoset resin impregnated surface layer bearing a decorative pattern carrying a coating which consists of a transparent thermoset resin in which is dispersed quartz with a maximum particle size of 50 microns and fibrous material of length not exceeding 100 microns and of refractive index similar to that of the thermoset resin such that the coating is transparent.

2. A laminate according to claim 1, in which the average size of the quartz particles is 2—50 microns.

3. A laminate according to claim 2, in which the average size of the quartz particles is 10—15 microns.

4. A laminate according to any one of the preceding claims, in which the thermoset resin is a melamine-formaldehyde resin.

5. A laminate according to any one of the preceding claims, in which the coating contains, for each 100 parts by weight of thermoset resin, 5—30 parts of quartz and 10—40 parts of the fibrous material.

6. A laminate according to claim 5, in which the coating contains 10 parts of quartz and 20 parts of fibrous material.

7. A laminate according to any one of the preceding claims, in which the fibres of the fibrous material are 30—50 microns long.

8. A laminated according to claim 1 substantially as hereinbefore described.

9. A process for the production of a laminate claimed in any one of the preceding claims which comprises applying to a thermosetting resin-impregnated sheet or layer carrying a decorative pattern a coating composition comprising the thermosetting resin, the quartz and the fibrous material and subsequently curing the said resin by subjecting a laminate assembly containing the coated sheet or layer at the surface to heat and pressure.

10. A process according to claim 9, in which the volatiles content of the coated resin-impregnated decorative layer is reduced to at most 5%.

11. A process according to claim 9 or 10, in which the coating composition contains also a penetration control additive.

12. A process according to claim 11, in which the said additive is an alginate.

13. A process according to any one of claims 9—12, in which the coating composition is applied to the decorative layer in amount to provide a coating weight of between 90 and 110 grams per square metre.

14. A process according to any one of claims 9—13, in which the decorative sheet is impregnated with a thermosetting resin immediately before the coating composition is applied thereto.

15. Process according to claim 9 substantially as hereinbefore described.

16. A laminate according to any one of claims 1—8 when produced by a process claimed in any one of claims 9—15.

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